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⑲ Ⓒ **CANADIAN PATENT** ⑫

�54 PROCESS FOR PRODUCTION OF FINELY DIVIDED
MAGNETITE PARTICLES

㊙ Kunda, Wasyl; Rudyk, Boris,
           Canada

Granted to Sherritt Gordon Mines Limited,
            Canada

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A B S T R A C T

     Finely divided particles of magnetite are
produced by mixing solutions containing ferrous ions, ferric
ions and free ammonia in proportions necessary to neutralize
any free acid. The mixture is maintained at a temperature
of at least $50^{\circ}C$. Magnetite particles precipitate from
the mixture and may be recovered by conventional liquid-
solid separation procedures.

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This invention r lates to a process for the
production of fine particles of magnetite suitable for use
in magnetic tapes and ink and the like. More particularly,
the invention relates to a process which involves reacting

5   ferrous and ferric salts, and ammonia under controlled
conditions in an aqueous medium to cause precipitation of
spheroidal, fine particles of magnetite.

It is known to prepare particles of magnetite by
subjecting iron powder to partial oxidation or by subject-

10   ing particles of hematite to partial reduction. The
magnetite particles thus produced are too coarse for use
in magnetic inks and must be pulverized by some means.
The means conventionally used for doing so is wet grinding
in a ball mill. However, grinding must be continued for a

15   very long time, frequently as long as 1,000 hours, to
decrease the state of subdivision of the particles to that
suitable for use in magnetic ink. Because of the prolonged
grinding required, the cost of the grinding operation is
considerable and usually accounts for a substantial portion

20   of the overall cost of production of the magnetite particles.

It is an object of the present invention to
provide a process by which spheroidal magnetite particles
suitable for use in magnetic inks and tapes can be produced
but which does not involve grinding the particles.

25   It is another object to provide a process by which
the size of magnetite particles can be controlled within the
range of 200 to 500Å by simple and inexpensive means.

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These and other objects may be accomplished by
a process which involves providing solutions containing
ferrous ions, ferric ions, and free ammonia; mixing said
solutions in proportions necessary to neutralize any free
acid; maintaining the temperature of the mixture at at
least $50^{\circ}C$ to cause a reaction therein with resulting
formation of finely divided particles of magnetite; and
recovering said magnetite particles.

The process of the invention is described below

10   with reference to the drawings in which:

Figure 1 is a graph showing the effect of the
mixing sequence of ammonia and aqueous
solutions of ferrous and ferric sulphate
on the settling rate of magnetite
precipitated from the resulting slurry;
and

Figure 2 is a graph showing the effect of the
Fe^{+++}/Fe^{++} molar ratio on the settling
rate of magnetite from a slurry of ferrous

20   hydroxide and ammonia to which is added
an aqueous solution of ferric sulphate.

As starting materials for the process of the
subject invention, solutions containing free ammonia and
dissolved salts of di- and tri-valent iron are required.
Three separate solutions may conveniently be used for the
purpose, one a solution which contains ferrous ions (for
the sake of brevity referred to below as solution 1), a
solution which contains ferric ions (solution 2) and a
solution which contains free ammonia (solution 3). Solutions

30   (1) and (2) may be derived from the combination of iron

values and one or more of the common acids in which the
iron values are soluble. The acid may, for example, be
sulphuric acid, hydrochloric acid and acetic acid.

The first step of the process involves mixing

5   solutions (1), (2) and (3) in such quantities that all free
acid in solutions (1) and (2) are neutralized by the free
ammonia in solution (3). In addition, it is preferred
that solutions (1) and (2) be combined in such proportions
that the ferric to ferrous molar ratio in the resulting

10   mixture be in the range of 3:1 to 1:1 and more perferably
2:1. It is also preferred that solutions (1), (2) and (3)
be so combined that the concentration of soluble iron values
in the mixture be in the range of 10 to 30 g.p.l.

The most convenient method for determining the

15   correct amount of solution (3) which must be combined with
solutions (1) and (2) to neutralize all free acid is to
monitor the pH of the resulting mixture. All free acid
will be neutralized when the pH of the mixture is the same
or higher than the pH of the iron salt resulting from the

20   reaction between the iron values and the acid in solutions
(1) and (2). For example, should the acid in solutions (1)
and (2) be sulphuric acid, a sufficient quantity of
solution (3) should be added to increase the pH to at
least 5.4 which is the pH of iron sulphate in solution.

25   Similarly, should the acid be acetic acid, solution (3)
should be added in sufficient quantity to increase the pH
to that of iron acetate in solution. In cases where the
form of the iron salt in solutions (1) and (2) is unknown
because, for example, the acid make-up of solutions (1)

30   and (2) is undetermined, the quantity of solution (3) with

solutions (1) and (2) should be that required to raise the pH to about 7. It is possible to raise the pH to a higher value but it is preferred not to do so because of the added cost of handling a more basic mixture and because of the tendency of the magnetite formed in the mixture to oxidize to iron hydroxide.

As indicated above, it is preferred to maintain the Fe^{+++}/Fe^{++} molar ratio in the mixture resulting from the combination of solutions (1), (2) and (3) within the range of 3:1 and 1:1. Where the molar ratio is outside this range, undesirably large quantities of iron hydroxide are formed in the mixture with resulting lowering of the magnetic properties of the end product of the process. It should be noted, however, that the lowering of magnetic properties is more pronounced where the ferric to ferrous molar ratio is below 1:1 than where it is above 3:1.

In general, the overall concentration of iron in the mixture has no effect on the formation of magnetite. However, an iron concentration below about 30 g.p.l. favours production of a finer magnetite product than a higher concentration of iron. Since a finer product is generally more useful than a coarser product, it is preferable to maintain the concentration of iron below 30 g.p.l.

The sequence of mixing solutions (1), (2), and (3) has a significant effect on the quantity of magnetite produced by the subject process. The mixing of ferrous solution (1) and ferric solution (2) and the addition of the resulting mixture to ammoniacal solution (3) causes an immediate reaction in which substantially all iron values present in the mixture or slurry convert to magnetite.

Even more rapid and complete conversion of the soluble iron
values to magnetite occurs when the ferrous-ferric mixture
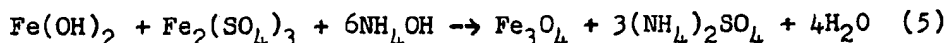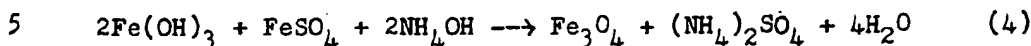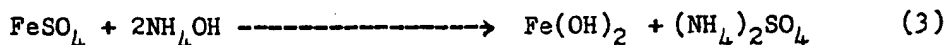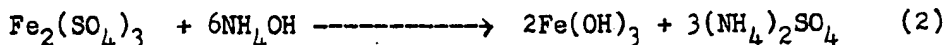is sprayed into ammoniacal solution (3).

The addition of ammoniacal solution (3) to a
ferrous-ferric solution (1) (2) results in the precipitation
first of brown $Fe(OH)_3$, then the precipitation of green
$Fe(OH)_2$ and finally, magnetite. However, conversion of
$Fe(OH)_3$ and $Fe(OH)_2$ to magnetite is incomplete. The
addition of ferrous solution (1) to ammoniacal solution (3)
and afterward the addition of ferric solution (2) to the
resulting ferrous ammoniacal solution (1) (3) results first
in the precipitation of $Fe(OH)_2$ and afterward the precipitation
of magnetite but again conversion to the latter compound is
incomplete. Similarly, the addition of ferrous solution (1)
to a combined solution (2) and (3) results in the incomplete
conversion of soluble iron values to magnetite.

The temperature of the mixture or slurry resulting
from the combination of solutions (1), (2) and (3) should be
maintained at at least $50^{\circ}C$ and preferably should be main-
tained at a temperature within the range of from about 100 to
$150^{\circ}C$. Maintaining the temperature near the upper limit of
this range results in a magnetite end product which is
denser and which has a smaller surface area than the end
product produced at a lower temperature.

The reaction which is believed to occur in the
mixture or slurry is as follows (where solutions (1) and
(2) contain sulphuric acid):

$$Fe_2(SO_4)_3 + FeSO_4 + 8NH_4OH \longrightarrow Fe_3O_4 + 4(NH_4)_2SO_4 + 4H_2O$$

(1)

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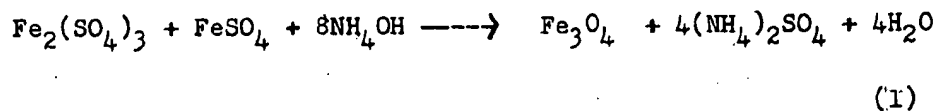
Besides this reaction, other side reactions are also believed to take place, they being:

$$Fe_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4 \quad (2)$$

$$FeSO_4 + 2NH_4OH \longrightarrow Fe(OH)_2 + (NH_4)_2SO_4 \quad (3)$$

5
$$2Fe(OH)_3 + FeSO_4 + 2NH_4OH \longrightarrow Fe_3O_4 + (NH_4)_2SO_4 + 4H_2O \quad (4)$$

$$Fe(OH)_2 + Fe_2(SO_4)_3 + 6NH_4OH \longrightarrow Fe_3O_4 + 3(NH_4)_2SO_4 + 4H_2O \quad (5)$$

As evident from the above equations, ammonia is essential to precipitation of magnetite. The minimum quantity of ammonia required is the stoichiometric equivalent

10   of the quantity of sulphate sulphur present in the combined solution. Thus 2 moles of ammonia are required for each mole of sulphate sulphur present. Ferric sulphate and ferrous sulphate solutions accordingly require 3 and 2 moles of ammonia per mole of iron respectively. In addition, 2

15   moles of ammonia are required for each mole of free sulphuric acid present in the combined solution. As previously indicated, the most convenient method for ensuring that sufficient ammonia is present in the mixture or slurry resulting from the combination of the three solutions is

20   by monitoring the pH thereof . When the pH is 5.4 or higher, no further ammonia need be added.

In general, agitation of the mixture results in a finer product; thus, the size of the final product can be, to a certain extent, controlled by the extent to which

25   the mixture is agitated during the reaction.

Various so-called "surface active agents" may be added to the mixture to control the shape and size of the precipitated magnetite particles. Agents suitable for the purpose are those identified by the trade marks Goulac,

30   Dextrin, Orzan, Tween 60, EMA-1103, Span 85 and Aerosol C-61. Usually a concentration of about 0.5 g.p.l. of the agent in the mixture is sufficient for the purpose.

At the completion of the reaction, the magnetite particles may be separated from liquid by filtration and may be dried by conventional means. During drying, the particles usually agglomerate but in most cases the

5   agglomerates may be broken down without difficulty. For example, where the particles are washed with water and dried at 100°C, they agglomerate into a very brittle lump but the lump can be easily broken down by grinding. Where the particles are washed in acetone and dried in a vacuum,

10   they agglomerate into a soft product which again may be broken down without difficulty.

        The resulting magnetite particles are generally spheroidal in shape and are within the size range of about 200 to about 500Å. The particles may be somewhat contami-

15   nated with iron hydroxide which can be converted to magnetite by heat treatment in a neutral atmosphere.

<div align="center">

EXAMPLE 1
</div>

        This example illustrates the effect which the sequence of mixing the ferrous solution (1), ferric

20   solution (2) and ammoniacal solution (3) has on the settling rate of precipitated magnetite. Samples of such solutions were mixed in various sequences to form a number of charges, each 700 ml in volume and containing 10 g.p.l. iron. The molar ratios of Fe^{++}, Fe^{+++} and NH_3 in the charges were:

25   $Fe^{+++}/Fe^{++} = 2:1$ and $NH_3/Fe_T = 4:1$. To some charges were added 0.5 g.p.l. EMA-1103, to others none. The charges were maintained at a temperature of 50°C for an hour each.

        Figure 1 illustrates the effect of the mixing sequence on the settling rate of precipitated magnetite.

30   The figure clearly shows that the settling rate is slowest

where the mixing sequence is solutions (1) and (2) added

to solution (3) and is fastest where the mixing sequence

is solution (1) added to a mixture of solutions (2) and

(3). It is believed that the solid product from the

former mixing sequence settles more slowly than the product

from the latter mixing sequence because the former product

is significantly finer than the latter product. Since a

finer product is preferred, the former mixing sequence is

preferred.

EXAMPLE 2

This example illustrates the effect of the

Fe^{+++}/Fe^{++} molar ratio on the settling rate of precipitated

magnetite. 700 ml samples were prepared by adding various

amounts of a solution containing ferric ions to a solution

containing free ammonia and ferrous ions. The total con-

centration of iron in the samples was approximately 10 g.p.l

and the NH_3/Fe_T molar ratio was 4. The surface activator

EMA-1103 was added to some of the samples.

The samples were maintained at a temperature of

$50^{\circ}C$ for a period of time and the settling rate of

magnetite from the samples was determined by periodically

measuring the height of the zone of clear solution above

the dark magnetite-containing slurry. The results are

shown in Figure 2.

From Figure 2 it is clear that the fastest settling

rate occurs when the Fe^{+++}/Fe^{++} ratio is 3:1 and the slowest

rate occurs when the ratio is 1:1. The slow settling rate

is believed to be due to the presence of $Fe(OH)_2$. Mag-

netite particles precipitated from samples containing EMA-1103

settled more slowly indicating that the particles were

probably somewhat finer than magnetite particles precipitated

from samples lacking the surface activator.

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The embodiments of invention in which an exclusive property or privilege is claimed are defined as follows:

1.   A process for producing finely divided particles of magnetite comprising: providing solutions containing ferrous ions, ferric ions and free ammonia; mixing said solutions in proportions necessary to neutralize any free acid; maintaining the temperature of the mixture at at least about $50^{\circ}C$ to cause formation of finely divided particles of magnetite; and recovering said magnetite particles.

2.   The process as claimed in claim 1 wherein the ratio of ferric ions to ferrous ions in said solutions is in the range of from about 3:1 to about 1:1.

3. -   The process as claimed in claims 1 wherein the ratio of ferric ions to ferrous ions in said solutions is 2:1.

4.   The process as claimed in claim 1 wherein the concentration of iron in said solutions is in the range of about 10 to about 30 g.p.l.

5 .   The process as claimed in claim 1 wherein the temperature of said solutions is maintained within the range of 100 to about $150^{\circ}C$.

6.   The process as claimed in claim 1 wherein said mixture also contains a surface active agent selected from the group consisting of Goulac, Dextrin, Orzan, Tween 60, EMA-1103, Span 85 and Aerosol C-61.✻

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✻ *trademark*

7.   A process for producing finely divided particles of magnetite comprising: providing a slurry derived from the combination of divalent and trivalent iron values dissolved in an acidic medium and sufficient ammonia to adjust the pH of the liquid in said slurry to that of an iron salt resulting from the reaction between said iron values and the acid; maintaining said slurry at a temperature of at least $50^{\circ}C$ to cause formation of finely divided particles of magnetite; and recovering said magnetite particles.

8.   A process for producing finely divided particles of magnetite comprising: providing (a) a starting solution containing ferrous ions and ferric ions in an acidic medium and (b) an ammoniacal solution; adding solution (a) to a sufficient quantity of said solution (b) such that all free acid in the resulting slurry is neutralized; maintaining said slurry at a temperature of at least about $50^{\circ}C$ to cause formation of finely divided particles of magnetite; and recovering said magnetite particles.

9.   The process as claimed in claim 8 wherein solution (a) is added to solution (b) by spraying.

10 .   The process as claimed in claims 7, 8 or 9 wherein the ratio of ferric ions to ferrous ions in said acidic medium is in the range of from about 3:1 to about 1:1.

11.   The process as claimed in claims 7, 8 or 9 wherein the ratio of ferric ions to ferrous ions in said acidic medium is 2:1.

12.   The process as claimed in claims 7, 8 or 9 wherein the concentration of iron in said acidic medium is in the range of about 10 to 30 g.p.l.

13.   The process as claimed in claims 7, 8 or 9 wherein the temperature of said acidic medium is maintained in the range of about 100 to about 150°C.

14.   The process as claimed in claims 7, 8 or 9 wherein said slurry also contains a surface active agent selected from the group consisting of Goulac, Dextrin, Orzan, Tween 60, EMA-1103, Span 85 and Aerosol C-61.*

15.   The process as claimed in claims 7, 8 or 9 wherein said acidic medium is sulphuric acid and the pH to which said slurry is adjusted is at least about 5.4.

* Trade mark

EFFECT OF MODUS OF MAGNETITE
PRECIPITATION ON SETTLING;

CONDITIONS: 50°C; 10gpl IRON; NONE OR 0.5gpl EMA-1103;
        Fe^{+++}/Fe^{++} MR= 2/1; NH_3/Fe MR=4/1;
        700ML CHARGE IN BEAKER.

MODUS OF SOLUTION MIXING:
    (a) AMMONIA ADDED TO THE MIXTURE OF
        Fe^{+++} & Fe^{++} SOLUTIONS.
    (b) Fe^{+++} & Fe^{++} SOLUTIONS ADDED TO AMMONIA SOLUTION
    (c) Fe^{+++} SOLUTION ADDED TO MIXTURE OF
        Fe^{++} & AMMONIA SOLUTIONS.
    (d) Fe^{++} SOLUTION ADDED TO A MIXTURE OF
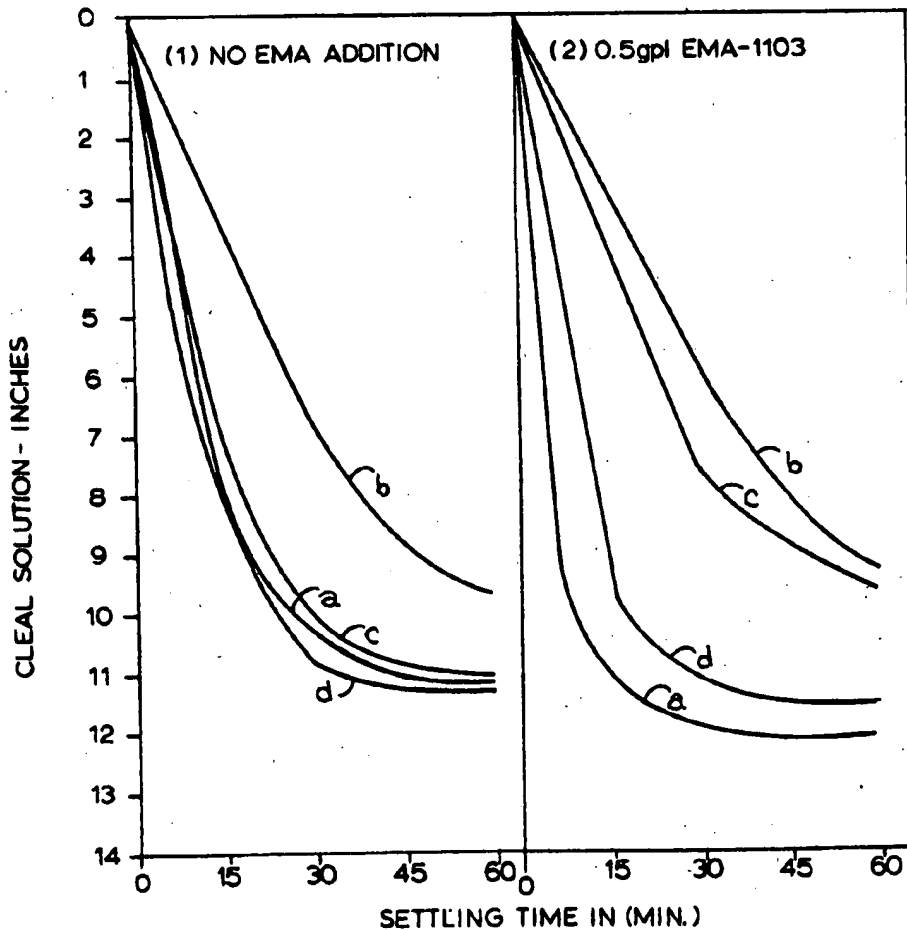 Fe^{+++} & AMMONIA SOLUTIONS.

FIG. 1

FORS A PIPER

EFFECT OF Fe^{+++}/Fe^{++} MOLAR RATIO ON
SETTLING OF MAGNETITE (1) IN ABSENCE OF
EMA-1103; AND (2) IN THE PRESENCE OF EMA-1103

CONDITIONS: 50°C; 10gpl IRON; NH3/Fe MR= 4;
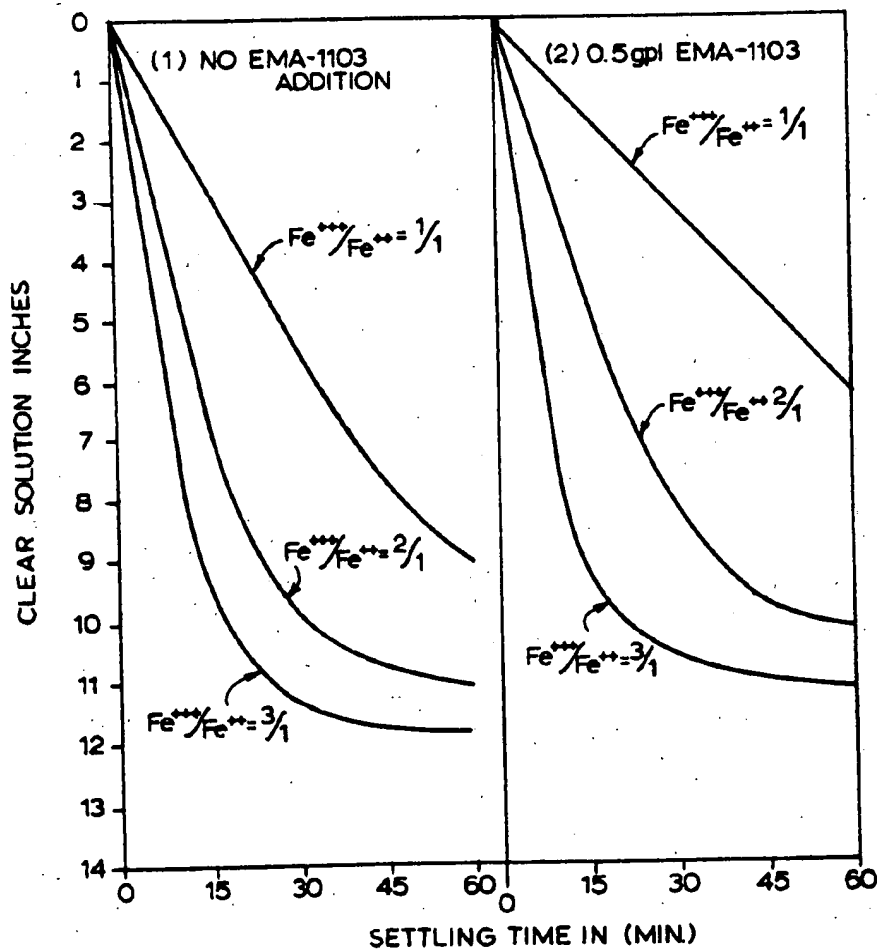METHOD-C; 700 ML CHARGE IN THE BEAKER.

FIG. 2

FORS A PIPER